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Electrical conductivities and dielectric constants of some sodium tetraborate glasses containing CuO, irradiated with a low-level fast neutron beam

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A number of glass samples were prepared from a mixture of $Na_2B_4O_7$ and CuO. The prepared glasses were irradiated with a low-level fast neutron beam (flux density 10^8 n cm^{-2}). The alternating current (a.c.)-electrical conductivity and the dielectric constant at a frequency of 1 kHz of these glasses have been studied as a function of temperature in the range 300–600 K. The measurements showed that an amorphous–crystalline phase transition characterized these samples. This phase transition was affected by neutron irradiation. Also a decrease in the activation energy for the irradiated undoped sample and an increase in the activation energy for the irradiated doped samples were found. After irradiation, the maximum peak, which characterized the dielectric constant of the samples before irradiation, disappeared. © *1998 Chapman & Hall*

1. Introduction

In recent years, extensive studies of the electrical and optical properties of semiconducting glasses containing transition metal ions (TMIs) have been reported [1–7 and references therein]. It is known that, in these glasses, the conduction mechanism is difficult to interpret. This mechanism is affected by numerous factors, including the nature and concentration of the TMIs in a reduced valence state, the propagation condition and the existence of microscopic and macroscopic structure within the glass matrix.

Recently, increasing attention has been paid to the investigation of the semiconducting properties of borate based glasses. For instance, the effect of CuO addition on the electrical properties of $Na_2B_4O_7$–Pb_3O_4 glasses has been reported [8]. In this report, it has been stated that conduction in this ternary system is electronic rather than ionic. Similar studies have been made for $Na_2B_4O_7$ containing both Fe_2O_3 [9] and CuO [10].

The objective of the present work, besides the study of a.c.-electrical conductivities and dielectric constants of some $Na_2B_4O_7$ glasses containing low concentrations of CuO, is to study the effect of neutron bombardment on the following

- magnitude of conductivity at room temperature,
- dielectric losses,
- location of the critical temperature,
- activation energies, and
- composition dependence of the a.c.-conductivity.

2. Experimental procedure

Sodium tetraborate glasses as a pure sample and samples containing 0.25 and 2 mol % CuO were prepared from chemically pure grades of material according to their molar compositions in an alumina crucible. A typical melt containing some 15 g of material, was stirred from time to time using an alumina rod and was melted at 1000 °C. Attention has been paid to reduce the mechanical and volatilization losses.

The molten glass was cast onto a stainless steel plate in the form of a circular disc of 2 cm diameter and 2 mm thickness. The samples were transferred immediately to another furnace and were annealed at 400 °C for 1 h. They were allowed to cool gradually to room temperature and were then polished.

The samples were irradiated at room temperature with fast neutrons from a ^{252}Cf source, with a flux density of 10^8 n cm^{-2}. The neutron fluence at the position of exposure was measured with the use of calibrated ^{115}LR-track detectors. Silver dag was used to make two circular electrodes placed on either side of each non-irradiated and irradiated sample.

The sample was placed between two copper electrodes and mounted inside an electric furnace with a maximum temperature of 1000 °C. The a.c.-electrical conductivity and the dielectric constant were measured as a function of temperature for each sample, using an automatic Wayne Kerr bridge model 900B at a constant frequency of 1 kHz. The temperature of the furnace was controlled by a stabilized variac. The measurements were made from room temperature

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to 600 K at a heating rate of 1 °C min^{-1}. The temperature of each sample was measured using a copper–chromel alumel thermocouple placed at the sample holder.

3. Results

In Table I, the values of the measured a.c.-electrical conductivities, $\sigma_{a.c.}$, at a constant frequency of 1 kHz at room temperature for the non-irradiated and irradiated pure $Na_2B_4O_7$ glass sample (sample 1) and samples containing 0.25 and 2 mol % CuO (samples 2 and 3, respectively) are presented. In Fig. 1a–c, the variation of ln $\sigma_{a.c.}$ as a function of reciprocal temperature for the non-irradiated (curve 1) and irradiated (curve 2) glass samples are illustrated.

From Table I, it is worth noting that the non-irradiated $Na_2B_4O_7$ glass doped with a low CuO concentration of 0.25 mol % exhibits a decrease in its conductivity by two orders of magnitude compared with the conductivity of the pure sample. While a slight decrease in the conductivity for the sample containing 2 mol % CuO is observed. A similar effect in sodium tetraborate glasses containing Fe_2O_3 has been reported [9]. For the irradiated samples, the conductivities all show the same order of magnitude, i.e. $10^{-7}\,\Omega\,m^{-1}$.

The curves in Fig. 1 consist of three different stages. In the induction (amorphous) stage a fast increase in the conductivity with increasing temperature is obtained. In the stage prior to crystallization, the conductivity decreases with increasing temperature. It reaches a minimum value at the phase transition temperature, T_c. These minimum values and the phase transition temperatures for all samples are given in Table II.

In the crystalline stage above the phase transition temperature, a straight line characterizes the relation between ln $\sigma_{a.c.}$ versus $1/T$(K). Which satisfies the formula

$$\sigma_{a.c.} = \sigma_0 \exp\left(\frac{-E_{cryst}}{kT}\right). \quad (1)$$

where E_{cryst} is the activation energy in the crystalline state and k is the Boltzman constant.

The values of E_{cryst} for all samples are listed in Table III. An activation energy of 0.74 eV is obtained for the non-irradiated $Na_2B_4O_7$ pure glass sample. This value is to be compared with the corresponding values of 0.55 and 1.35 eV reported in [9] and [10], respectively.

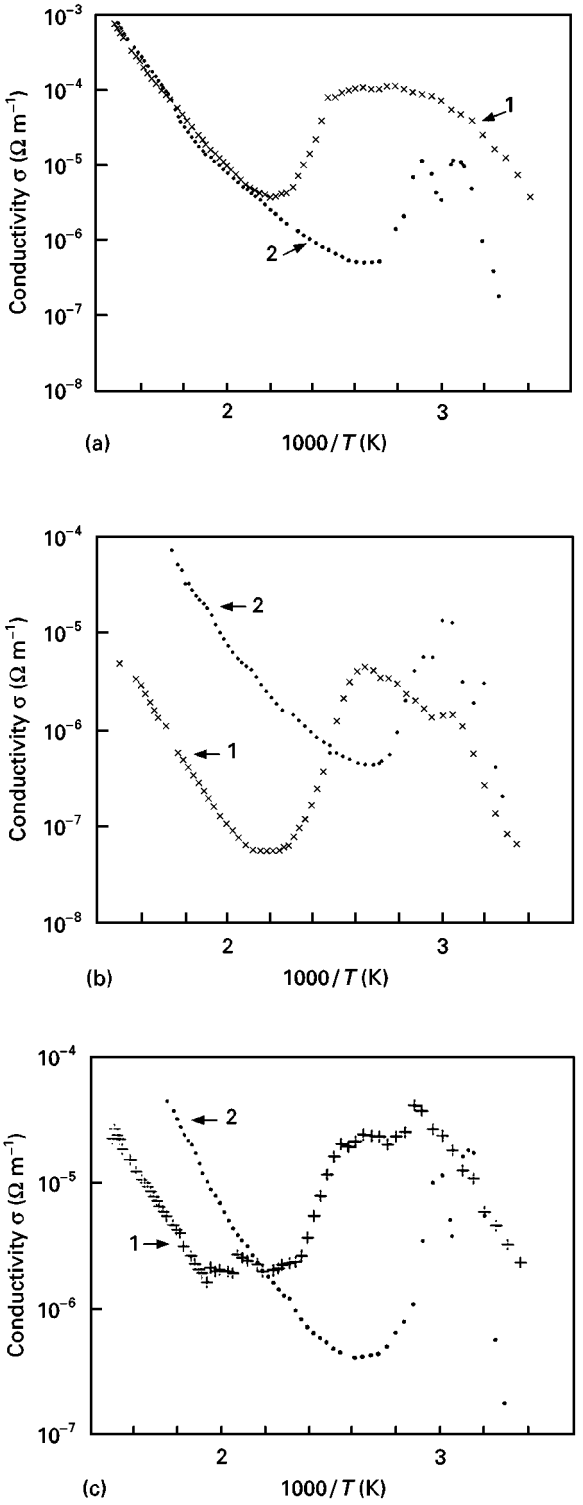

Figure 1 The natural logarithm of a.c.-electrical conductivity at a frequency of 1 kHz as a function of $1/T$ (K) for the non-irradiated (+) and irradiated (●) samples: (a) sample 1, (b) sample 2, and (c) sample 3.

TABLE I Values of a.c.-electrical conductivities, $\sigma_{a.c.}$, at room temperature for non-irradiated and irradiated samples

Samples	Composition (mol %)		$\sigma_{a.c.}$ $(\Omega\,m)^{-1}$	
	$Na_2B_4O_7$	CuO	Before irradiation	After irradiation
1	100	0.0	1.4×10^{-5}	1.9×10^{-7}
2	99.75	0.25	6.8×10^{-8}	2.1×10^{-7}
3	98	2.0	2.6×10^{-6}	2.0×10^{-7}

TABLE II Minimum values of a.c.-electrical conductivities, $\sigma_{a.c.}$, and corresponding phase transition temperatures, T_c

Sample	Before irradiation		After irradiation	
	$\sigma_{a.c.}$ $(\Omega\,m^{-1})$	T_c (K)	$\sigma_{a.c.}$ $(\Omega\,m^{-1})$	T_c (K)
1	3.9×10^{-6}	453	5.2×10^{-7}	377
2	5.6×10^{-8}	468	4.5×10^{-7}	377
3	2.0×10^{-6}	488	4.4×10^{-7}	383

TABLE III Activation energies in the crystalline matrix for non-irradiated and irradiated samples

Sample	Activation energy (eV)	
	Before irradiation	After irradiation
1	0.74	0.51
2	0.51	0.58
3	0.49	0.57

From Table III, it is noticed that the values of E_{cryst} for the non-irradiated samples decrease with increasing CuO content. A similar effect has been discussed in [10], where direct current (d.c.)-conductivity of non-irradiated $Na_2B_4O_7$ glasses doped with CuO at different concentrations (5–20 mol %) were studied in the temperature range 293–573 K. Experimental data of the electrical conductivities of these samples were found in the temperature range between 450 and 573 K. This temperature range only covers the variation of conductivity within the crystalline matrix of these samples, as discussed above. For this reason, the measurements presented in [10] should be extended to cover the whole temperature range (293–573 K) for comparison.

In Fig. 2a–c, the variation of dielectric constant, ε, as a function of temperature at a constant frequency of 1 kHz is shown for the non-irradiated (curve 1) and irradiated (curve 2) glass samples, numbers 1–3, respectively.

It is noticed that, the value of ε for all samples has a maximum peak at 378 K for all non-irradiated samples (Fig. 2, curve 1). These peaks occur when the phase velocity of the phonon within the glass matrix is larger than the thermal velocity of the electron. In such a situation, the free electrons cannot adjust rapidly enough to the screened lattice potential. Therefore, the build-up of charge results in the enhancement of the interaction with other electrons. This phenomenon is known as an anti-screening effect.

The maximum values of ε for all non-irradiated samples are collected in Table IV. It is worth mentioning that adding CuO with a concentration of 0.25 mol % leads to a three-fold increase of ε, the corresponding ε value of the pure sample 1. Increasing the CuO content to 2 mol % leads to an increase of the conducting electrons, consequently causing a decrease in the ε value.

The effect of neutron bombardment at a flux density of 10^8 n cm^{-2} on the $Na_2B_4O_7$ pure glass (sample 1) was obvious from the colour, of the sample which changed from colourless to yellowish, in this case five different features were observed, namely

1. The value of conductivity at room temperature decreased by two orders of magnitude compared with the corresponding value of the non-irradiated sample 1 (Table I).
2. Another phase clearly appeared at a temperature of 333 K, as seen from Fig. 1a, curves 1 and 2.
3. The crystalline phase transition temperature shifted towards lower temperature (Table II).

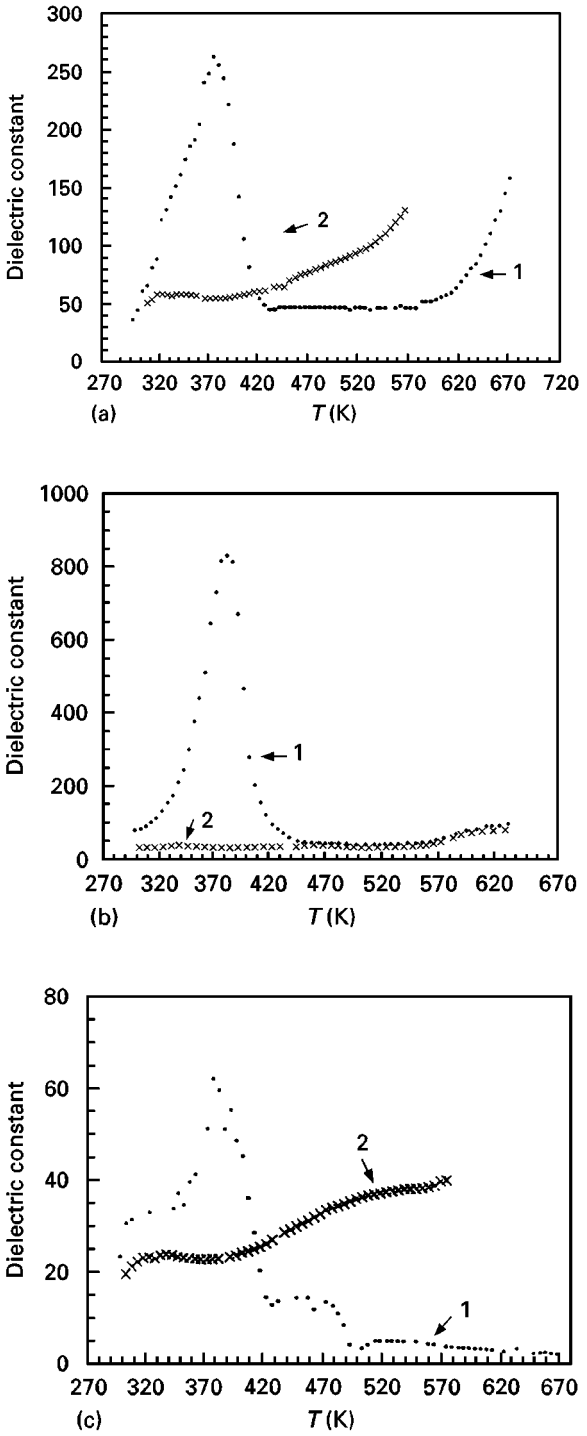

Figure 2 The value of the dielectric constant, ε, at a frequency of 1 kHz as a function of temperature for the non-irradiated (•) and irradiated (×) samples: (a) sample 1, (b) sample 2, and (c) sample 3.

TABLE IV Peak positions and values of the dielectric constant, ε, for non-irradiated samples

Sample	ε	T (K)
1	263	378
2	832	378
3	062	378

4. The activation energy characterizing the crystalline matrix decreased by 30% in comparison with the corresponding value for the non-irradiated sample (Table III).

5. The maximum peak of the dielectric constant characterizing the non-irradiated sample 1 disappeared.

For the doped samples 2 and 3 the blue colour became darker after irradiation. Also, neutron bombardment led to a change in conductivity at room temperature. Moreover, the phase transition temperature shifted towards lower temperatures and the activation energy characterizing the crystalline matrix of these samples increased by 12 and 16%, respectively, compared with the corresponding value of the non-irradiated doped samples.

4. Discussion

From Fig. 1a (curve 1), the observed increase in conductivity of the non-irradiated sample 1 with increasing temperature, is attributed to thermal agitation, which facilitated the movement of Na^+ ions in the interstices of the boron network. It is worth noting that a slight variation in conductivity occurred just before the stage prior to crystallization indicating the existence of another phase in this temperature region.

The decrease in conductivity in the stage prior to crystallization is attributed to the microstructural changes associated with heat treatment during the annealing process. In the crystalline matrix, the increase of conductivity with temperature is attributed to the transformation of BO_4 ions into BO_3 ions. Therefore, the energy activating the crystalline stage is the energy needed to activate ion diffusion and separate one configuration of the borate unit from another. The addition of CuO to sodium tetraborate is considered in this study to be a modifier. This CuO leads to an increase in the electronic conduction of the doped samples. Actually, electronic conduction in semiconducting glasses is often due to the presence of TMIs of different valances.

It has been stated that, if there are two elements in a glass system, which form ions of variable valence, then interaction between these ions usually takes place [5]. Consequently, Cu^+–Na^+ interaction explains the influence of CuO addition on the decreasing conductivity of the pure $Na_2B_4O_7$ sample.

The decrease in activation energy of pure non-irradiated $Na_2B_4O_7$ following addition of CuO within the crystalline matrix is attributed to the hoping electrons from the low valence state of Cu^+ to the higher valence state of Cu^{2+}. Then the change in CuO content in the glass composition alters the ratio (Cu^+/Cu_{Total}). This variation could control the transition probabilities of the conduction electrons, hence lower the activation energy.

At this point more theoretical studies are needed in order to explain the effect of neutron radiation on the electrical properties of such glasses.

5. Conclusions

From the measurements of a.c.-electrical conductivity and dielectric constant as a function of temperature for some $Na_2B_4O_7$ glasses as a pure sample and samples containing 0.25 and 2 mol % CuO, irradiated with a low-level neutron beam of flux density 10^8 n cm^{-2}, the following observations are made

1. At room temperature, the conductivity depends on the CuO concentration of the non-irradiated samples, while it is independent of CuO content for the irradiated glasses.
2. An amorphous–crystalline phase transition occurs at temperatures of 453, 468 and 488 K in the non-irradiated samples. The location of these temperatures was shifted to 377, 377 and 383 K for the irradiated samples.
3. The conductivity within the crystalline matrix follows Abraham's formula for all measured samples.
4. After irradiation a decrease in the activation energy by 30% for the pure sample and an increase in the activation energy by 12 and 16% for the glasses containing 0.25 and 2 mol % CuO occurs.
5. After irradiation, the maximum peak characterizing the dielectric constant of all non-irradiated glasses disappears.

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